A Facile Preparation of Benzaldehyde Diaryl Acetals

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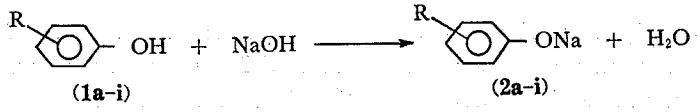
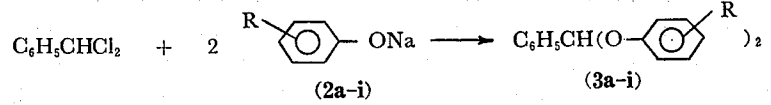
Several benzaldehyde diaryl acetals were prepared in excellent yields by treating sodium phenolates with benzylidene dichloride in dimethyl sulfoxide under mild conditions. These acetals will be cumbersome to prepare by other synthetic methods.

Dimethyl sulfoxide (DMSO) is one of the most widely employed and most effective solvents for nucleophilic substitution reaction.[1] The nucleophilic enhancement of anions by it is well known. The reactions of several *gem*- and *vic*-polychloroethanes containing 3-5 chlorine atoms with sodium phenolate in DMSO (or with sodium thiophenolate in N, N-dimethylformamide) have been demonstrated by Tanimoto and coworkers.[2] This procedure afforded either the mono-, di- or tetrasubstituted compounds of polychloroethylenes by phenoxyl group (or phenylthio group) as the main products. A recent report[3] from our laboratory described a new synthetic method to formaldehyde diaryl acetals, in which dichloromethane was reacted with sodium phenolates in DMSO under extremely mild conditions to give moderately good yields of the acetals. The employment of DMSO facilitated the reaction, which had been known to require a high-pressure handling at an elevated temperature, to proceed even at ambient temperature under atmospheric pressure. We report here an extension of this method to the synthesis of several benzaldehyde diaryl acetals (**3a-i**), a new kind of acetals, which will be cumbersome to prepare by other synthetic methods. This synthesis uses readily

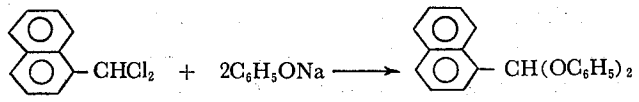


(1a-i) **(2a-i)**



(2a-i) **(3a-i)**

(a) R=H, **(b)** R=*o*-CH_3, **(c)** R=*m*-CH_3,
(d) R=*p*-CH_3, **(e)** R=*p*-CH_3O, **(f)** R=*p*-Cl,
(g) R=*p*-Br, **(h)** R=*m*-NO_2, **(i)** R=*p*-NO_2



(2a) **(3j)**

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Table I. Synthesis of Benzaldehyde Diaryl Acetals[a]

Run	R	Procedure	Reaction time (hr)	Product[b]	Method of purification	Yield[c] (%)
1	H	A	10	**3a**[d]	D	80
2	*o*-CH_3	A	10	**3b**[e]	CC	22
3	*m*-CH_3	A	10	**3c**[f]	D	68
4	*m*-CH_3	B	10	**3c**[f]	D	49
5[g]	*p*-CH_3	A	10	**3d**[h]	D	85
6	*p*-CH_3	B	10	**3d**[h]	D	70
7	*p*-CH_3O	A	7	**3e**[i]	D	78
8	*p*-Cl	A	20	**3f**[j]	D	69
9	*p*-Br	A	20	**3g**[k]	D	68
10	*m*-NO_2	A	20	**3h**[l]	R	60
11	*p*-NO_2	A	20	**3i**[m]	R	53
12[n]	H	A	10	**3j**[o]	R	96

a) All the reactions were carried out at 70°C unless otherwise noted. b) Satisfactory elemental analysis were obtained for all compounds. c) Represents isolated yield. d) Benzaldehyde diphenyl acetal (**3a**) was prepared previously by boiling benzylidene dibromide with an excess of phenol in a solution of pyridine, but the yield was extremely poor (0.7%).[4] Bp161-162°C/0.6 mmHg (lit.[4] mp 55-56°C). NMR ($CDCl_3$) δ 6.66 (s, 1H), 6.81-7.21 (*m*, 15H). e) Mp 67-70°C (ethanol). NMR ($CDCl_3$) δ 2.20 (d, 6H), 6.60-7.50 (*m*, 14H). f) Bp 183-185°C/2 mmHg. NMR ($CDCl_3$) δ 2.22 (s, 6H), 6.50-7.80 (*m*, 14H). g) Reaction temperatures varying in Run 5 from 70°C to 50°C or to 25°C resulted in a decreased yield of benzaldehyde di-*p*-tolyl acetal (**3d**) (64% or 43%). h) Bp 177°C/0.65 mmHg. NMR ($CDCl_3$) δ 2.22 (s, 6H), 6.57 (s, 1H), 6.80-7.70 (*m*, 13H). i) Bp 201°C/0.6 mmHg. NMR ($CDCl_3$) δ 3.71 (s, 6H), 6.49 (s, 1H), 6.86 (*m*, 8H), 7.20-7.65 (*m*, 5H). j) Bp 190°C/0.5 mmHg. NMR ($CDCl_3$) δ 6.60 (s, 1H), 6.75-7.70 (*m*, 13H). k) Bp 219°C/0.6 mmHg. NMR ($CDCl_3$) δ 6.60 (s, 1H), 6.75-7.65 (*m*, 13H). l) Mp 118-119°C (ethanol). NMR ($CDCl_3$) δ 6.98 (s, 1H), 7.35-8.10 (*m*, 13H). m) Mp 124-125°C (ethanol). NMR ($CDCl_3$) δ 6.91 (s, 1H), 7.05-8.25 (*m*, 13H). n) 1-Dichloromethylnaphthalene was employed in place of benzylidene dichloride. o) Mp 75-78°C (ethanol). NMR ($CDCl_3$) δ 7.00-8.40 (*m*, 18H).

available benzylidene dichloride together with sodium phenolates (**2a-i**) and also DMSO as solvent.

As indicated in Table I, the yield varies widely, depending on the structure of the monohydric phenols. For instance, the relatively poor yield was obtained with **2i**. This forms a contrast to the excellent yield with **2d**. It is likely that an inductive effect of substituent present in the benzene ring of phenol influences this reaction, and that the considerably poor yield with **2b** can be attributed mainly to steric effect.

In the preparation of benzaldehyde di-*m*-tolyl acetal (**3c**) and benzaldehyde di-*p*-tolyl acetal (**3d**), procedure A is superior in yields to procedure B (compare Run 3 with Run 4, and Run 5 with Run 6, respectively), but the latter procedure is more easier in handling, because it can be conducted without the trouble to previously prepare the sodium phenolates.

It was also recognized that the change of solvent from DMSO to acetonitrile or to dioxane causes an extreme lowering in yield of the acetals. For instance, when 4.0 g (25 mmol) of benzylidene dichloride was reacted with 6.5 g (50 mmol) of **2d** in acetonitrile (35 ml) at 70°C for 10 hr, an 18% yield of **3d** was isolated. The by-product, aside from the unchanged starting benzylidene dichloride (1.6 g), was a 12% yield of benzaldehyde. If the reaction was carried out in dioxane solvent (30 ml) instead of

acetonitrile, the yield of **3d** was less than 0.5%, and the others were also benzaldehyde (10%) and the starting benzylidene dichloride (2.4 g).

EXPERIMENTAL

Procedure A. A 100 ml, four-necked, round-bottomed flask, equipped with addition funnel, reflux condenser, thermometer and magnetic stirring bar, was charged with 50 mmol of a sodium phenolate and 20 ml of DMSO. The mixture was gently warmed up to 70°C with stirring to dissolve most of the sodium phenolate. To the nearly homogeneous solution was added slowly 25 mmol of benzylidene dichloride at 70°C. After addition, the reaction mixture was stirred for appropriate time at that temperature, after which the mixture was poured into a large quantity of aqueous sodium chloride solution. The mixture was extracted with three 100 ml portions of chloroform, and the chloroform solution was dried over anhydrous magnesium sulfate. Removal of the solvent afforded the crude reaction product, which was purified by distillation (D) *in vacuo* or by recrystallization (R) from ethanol. For the isolation of pure benzaldehyde di-*o*-tolyl acetal (**3b**), there was need of chromatographic procedure (CC) on silica gel (eluant: dichloromethane)

Procedure B. The reaction was conducted in a similar way, except that 50 mmol of phenol and 50 mmol of sodium hydroxide was charged in place of the previously prepared sodium phenolate in procedure A.

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